

EXPLORING STRUCTURAL BOND ENERGY RELEASE (SBER) IN NANODIAMONDS USING QUANTUM MOLECULAR DYNAMICS AND STATIC HIGH PRESSURE

William D. Mattson,* Radhakrishnan Balu, Betsy M. Rice, and Jennifer A. Ciezak
US Army Research Laboratory, AMSRD-ARL-WM-BD,
Aberdeen Proving Ground, MD 21005

ABSTRACT

We present a combined experimental and theoretical study on carbon nanodiamonds using Raman and DAC experimentation and *ab initio* calculations. Our calculations confirm the surface reconstruction to a fullerene-like structure, and indicate compression of the diamond core, producing an estimated internal pressure of 50 GPa. Quantum molecular dynamics simulations of hypervelocity collisions of NDs show that upon collision shock-induced amorphization first occurs, followed by complete disruption of the ND surface and ejection of reactive particles into the vacuum. Raman spectra of oxidized ND samples at increasing pressures showed a subtle increase in the vibrational intensity of the Raman feature centered near 1335 cm^{-1} near 18 GPa and continued under subsequent pressure increases. The intensification of this vibrational feature is consistent with a thinning of the amorphous carbon outer shell, which results in greater exposure to the diamond core with increasing pressure and may be a precursor to SBER initiation. Additionally, a nearly two-fold increase in the vibrational intensity of the sp^2 graphite peak centered near 1630 cm^{-1} in the spectra of the oxidized nanodiamond sample suggests the possibility of a sluggish partial phase transition from sp^3 hybridized diamond to sp^2 hybridized graphite.

1. INTRODUCTION

Immediate threats faced by the DoD demand superiority in lethality and survivability of its platforms and personnel. Current capabilities, developed for Cold War battles, do not address the changing nature of today's international conflicts. As a result, research and development (R&D) communities face an unprecedented challenge to transform the Army into a force that can dominate the full spectrum of military operations. The formulation of advanced energetic materials (EMs) used in critical defense areas is a key component that affects both lethality and survivability in both logistical and tactical environments. Current candidates considered as potential advanced EMs have known functionality and are synthesized using traditional concepts of inorganic and organic chemical synthesis. It is unlikely such compounds will produce materials with much more available energy than conventional EMs [Dlott, 2004].

Additionally, it is not yet possible to tailor the dynamic response of EMs that would permit optimal performance with minimal vulnerability for a wide range of future gun, missile, warhead, active protection systems, and emerging weapons concepts. These factors call for the development of completely new types of EMs that will produce revolutionary advances in energy release while maintaining acceptable vulnerability characteristics. Unless radically new methods are developed for increasing molecular strain using standard synthesis methods, the focus of R&D within the DoD must shift to largely unexplored areas such as those that involve chemical energy trapping and storage in currently unexploited types of metastable states. Such energy storage and conversion concepts have the potential to yield materials with energies several orders of magnitude larger than conventional explosives. Subsequently, these materials could provide enhanced or configurable performance in advanced weapons applications.

There are many simple stable materials that can transition to lower energy states through a solid-solid phase transition. Under most conditions, these transitions are so slow that no useful work is obtained from the corresponding energy release. However, in principle, energy can be stored in the structure and released upon transition. This little known phenomenon is referred to as Structural Bond Energy (SBE) [Tananaev, et al., 1987; Dlott, 2004] and in some cases, the stored structural potential energy can be liberated so rapidly that explosion occurs, termed structural bond energy release (SBER) [Al'tschuler, 1990 and 1991]. First documented in the United States by P.W. Bridgman in 1927, these experiments generated intense interest in the former Soviet Union, as evidenced by the numerous static and shock loading experiments exploring potential SBE materials such as carbon, silicon, borides and nitrides [Al'tschuler, 1990 and 1991]. Reports generated by Bridgman detail unusual explosive behavior of various inert materials, such as chalk and ice, when the material was subjected to high-pressure and shear [Bridgman, 1927 and 1935]. Experimental research in the United States has been absent since the 1960s [Teller, 1962], and it has only been in the past few years that interest has been revived, due to the advent of computational and experimental resources to fully explore the feasibility of the phenomena.

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In an earlier effort, we performed theoretical calculations to characterize high-pressure states (> 600 GPa) of a potential SBER material, carbon. We initially began searching for features in the phase diagrams of carbon that would suggest sharp thresholds for shock-induced polymorphic phase transition; our calculations began with the shock Hugoniot of diamond in order to see if any anomalies exist that might lead to the identification of new, high-pressure metastable phases of carbon. Although the equation of state and shock Hugoniot for graphite and diamond are well characterized at lower pressures, there are substantial gaps in our understanding at extremely high pressures.

In an earlier study, we presented the first Density Functional Theory (DFT) calculation of the shock Hugoniot of diamond [Romero and Mattson, 2007]. Our results are in excellent agreement with EOS models published by others over a wide range of pressures and temperatures. Our results provide new data for regions of the shock Hugoniot which were previously unknown to the scientific community, particularly in the lower pressure (< 140 GPa) and temperature (< 600 K) regime which is relevant to scientists who work with diamond-anvil cells (DACs). Furthermore, we produced results for the shock Hugoniot of diamond near the melt line in the warm dense solid phase where there is presently significant disagreement. While this earlier theoretical study has demonstrated that the theoretical calculations are adequate to reproduce existing experimental information on high pressure phases of carbon, we did not observe apparent anomalies in the shock Hugoniot for diamond that might lead to new, high pressure metastable phases that might confirm carbon as an SBER material.

However, during the course of the earlier theoretical investigation, we became aware of a combined experimental/theoretical study on surface reconstructions in nanodiamonds [Raty et al., 2003] that suggest such crystallites might contain significant SBE. The theoretical portion of this study used density functional theory (DFT) to predict the equilibrium structure of ND; the results indicated that surface reconstruction of ND of various sizes occurred, in which the surface atoms repositioned themselves into fullerene-type geometrical arrangements (Figure 1) spontaneously at low temperatures.

Both the experimental and theoretical results support the existence of these “bucky diamonds, i.e., carbon nanoparticles with a diamond core of a few nanometers and a fullerene-like surface structure” [Raty et al., 2003]. The calculations revealed tensile stress on the core of the nanocluster, implying that the reconfiguration of the fullerene like surface compresses the diamond core. Our own calculations of the diamond shock Hugoniot

[Romero and Mattson, 2007] indicate that very small degrees of compression produce huge increases in pressure. Thus, any subtle changes in the bonding structure of the outer shell that produce minor bond length modifications within the ND core could generate significant stored structural bond energy within the ND. In addition to the structural strain within the core, the interfacial strain between the fullerene-type shell and the diamond core may contribute to the total stored structural energy. These findings suggest that bucky diamonds may be potential SBER materials in that a sudden disruption of the shell and subsequent relaxation of the internal pressure of the core might result in the destruction of the diamond structure with an accompanying energy release. To explore this possibility, a joint experimental/quantum mechanical study explored the SBER phenomenon in ND. Quantum mechanical calculations using the Density Functional Theory (DFT) were performed to quantify the internal pressure and surface tension of the bare, reconstructed bucky diamonds. The results of these calculations are used to complement and guide experimental work focused on testing the feasibility of the SBER phenomenon with ND.

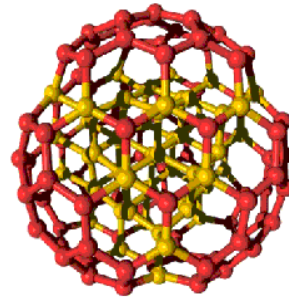


Figure 1. Fullerene-like surface of ND.

2. METHODS

Experimental: Piston-cylinder type diamond anvil cells with $300\ \mu\text{m}$ diamond culets were used for all static high-pressure experiments. Raw (NB-90) and Oxidized (NB90-OX) nanodiamond suspensions, were obtained from NanoBlox, Inc. The suspensions were dried in a drying oven at 150°C over the course of several days and then ground into a fine powder. A $60\text{-}100\ \mu\text{m}$ ND sample was loaded into the sample well ($\sim 120\ \mu\text{m}$ in diameter) of a rhenium gasket. The pressure within the diamond anvil cell was determined from the frequency shift of the ruby R_1 fluorescence line [Zha et al. 2000]. Raman spectra were obtained from an Ar^+ ion laser operating at $514.5\ \text{nm}$ with an optical system previously described [Goncharov et al. 1998] and a laser spot diameter of $\sim 4\ \mu\text{m}$ at room temperature. Prior to any experimental measurements, a wavelength calibration of the spectrograph was performed with a Neon lamp; this

method of calibration has an accuracy of $\pm 1 \text{ cm}^{-1}$. The spectral resolution for all Raman measurements was $\pm 4 \text{ cm}^{-1}$.

Theoretical: For all calculations, the Perdew-Burke-Ernzerhof PBE [Perdew et al, 1996] form of the Generalized Gradient Approximation (GGA) of the DFT and Goedecker-Teter-Hutter (GTH) pseudopotentials as implemented in the local orbital basis code CP2K [2008] were used. We employed the double zeta valence polarization (Gaussian) basis and an auxiliary plane wave basis with the kinetic energy cutoff of 400 Rydberg. The Gaussian and the plane wave bases remained consistent throughout the simulations. All the calculations were performed at the Γ points of the Brillouin zone as the unit cells were quite large. The SCF convergence tolerance at each step of the QMD calculations for all systems studied was 1×10^{-5} a.u. Snapshots of atomic positions at various times during the trajectory integrations were animated and analyzed using the visualization package VMD. [Humphrey et al. 1996]

Each ND was composed of 2052 atoms and an initial optimized geometry was obtained by cleaving a sphere out of bulk diamond with a diameter of 2.6 nm. The ND was allowed to relax in QMD simulations in the NVT ensemble ($T=300 \text{ K}$) in a simulation cell with edge length of 121.5 bohr. This large simulation cell was used to provide sufficient vacuum such that the periodic boundary conditions imposed in the simulations would not influence the equilibration of the single particle.

The reference system propagator algorithms (RESPA) implementation of the microcanonical ensemble implemented in CP2K was employed for the simulations of the collision. Trajectories of off-center collisions were performed using a step size of 1 fs. In order to simulate a hyper-velocity collision, atomic velocities for the colliding ND were assigned velocities above thermal to correspond to 10 km/sec, allowing for a 20 km/sec relative collision velocity.

3. RESULTS

Experimental: The Raman spectra of the Raw (RND) and Oxidized (OND) on isothermal compression ambient to 53 GPa are shown in Figures 2 and 3, respectively. There have been several Raman studies of micro- and nanocrystalline diamond prepared by CVD [Tolbert and Alivisatos, 1995; Bachman and Wiechert, 1992] but comparably few studies detailing the spectroscopic differences between various ND forms [Lipp et al., 1997 and references therein; Mykhaylyk, et al., 2005].

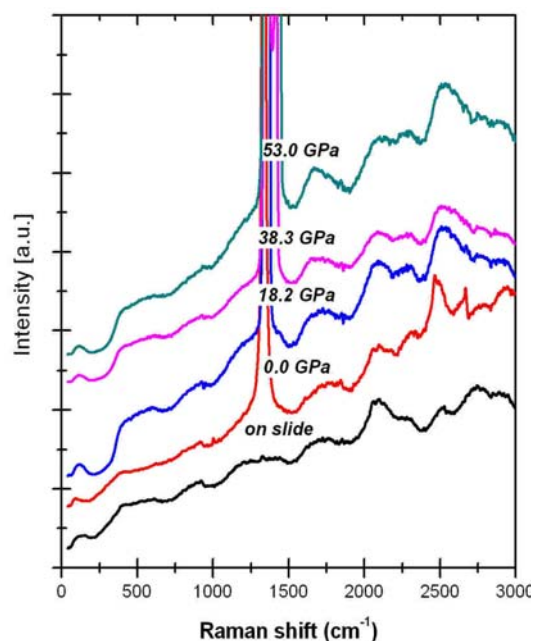


Figure 2. Raman spectra of raw nanodiamonds as a function of pressure. Spectra are shifted for viewing ease.

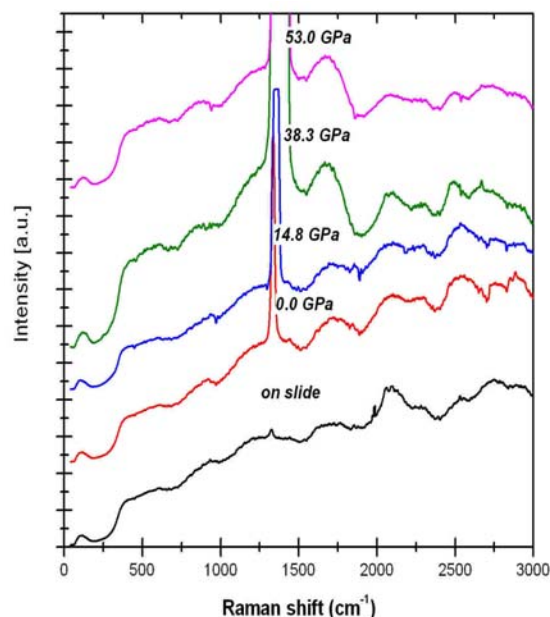


Figure 3. Raman spectra of oxidized nanodiamonds as a function of pressure. Spectra are shifted for viewing ease.

Although there are similarities between the Raman spectra of bulk single crystal (SC) diamond and micro/nanodiamond, due to the finite particle size of the ND obvious spectroscopic differences exist such as shifts in the vibrational frequencies and a generalized broadening of the bands [Yoshikawa et al., 1993; Bachmann et al., 1994]. These differences are readily apparent in Figures 2 and 3 where the sharp feature near 1330 cm^{-1} arises from the first order scattering from the

diamond (single crystal) anvils, and the remaining weak, broad features arise from the nanodiamonds.

The Raman spectra of both ND samples show the appearance of a broad shoulder ($\sim 1260\text{ cm}^{-1}$) on the low frequency side of the 1335 cm^{-1} SC feature near 15 GPa. Previous studies have shown the vibrational position of this shoulder lies within the spectral range associated with the partial density of states of the diamond lattice and indicates the nanodiamond particles have a composite structure consisting of a diamond core and an amorphous carbon shell [Mykhaylyk, et al., 2005]. At pressures near 15 GPa, the feature appears more intense in the RND but with increasing pressure the intensity in the corresponding OND spectra increases nearly two fold. The increase in the intensity of the OND feature is consistent with a thinner amorphous carbon surface structure, which would then expose the diamond core as pressure increases. An increase in the amount of exposed core is expected to be a precursor to an SBER event.

In addition to the sp^3 diamond feature, two very broad bands near 1000 cm^{-1} and between 1500 cm^{-1} and 1800 cm^{-1} are observed in the Raman spectra of both samples. The broad band between $1500 - 1800\text{ cm}^{-1}$ can be interpreted as a superposition of two peaks at 1630 cm^{-1} and 1750 cm^{-1} . The band near 1630 cm^{-1} is associated with sp^2 hybridized graphite while the 1750 cm^{-1} is thought to originate from C=O functionality on the ND surface [Mykhaylyk, et al., 2005]. These features are often observed in vibrational spectra of amorphous carbon samples that contain a high concentration of carbon atoms in mixed sp^2/sp^3 hybridization states [Ferrari and Robertson, 2001; Gilkes et al., 1997; Merkulov, et al., 1997]. Since the most probable end product of a ND SBER type phase transition is graphite, a transition would be indicated in the Raman vibrational spectrum by a sharp increase in the sp^2 peak centered near 1630 cm^{-1} . The intensity of this feature in the RND spectrum remains fairly consistent over the pressure range studied, indicating little to no transition occurs. This may be the result of thick amorphous carbon surface as well as the sample impurities. However, in the OND spectra, there is a nearly two-fold intensity increase in the sp^2 feature that correlates well with intensity increase of the 1260 cm^{-1} feature. This suggests a partial phase transition from sp^3 hybridized diamond to sp^2 hybridized graphite may be occurring, but it is sluggish.

Theoretical: DFT calculations were used to characterize a bare, reconstructed ND composed of 2052 atoms; the optimized structure of this ND is shown in Fig. 4. The bonds within the core were analyzed by calculating the average distance from an atom to its four nearest neighbors. These averages were then binned and averaged by the distance of the atom from the center of the nanodiamond. These bond lengths were then

compared to the bond lengths of bulk diamond to provide estimates of the internal pressure of the core by comparing local bond structure to that of bulk diamond at known pressure. Although the material near the surface is significantly distorted from that of bulk diamond, (see the equilibrium configuration shown in Fig. 4), the material within the core has the same coordination and orientation of the bonds as bulk diamond except the bonds are compressed to a point that corresponds to 50 GPa in compressed bulk diamond. Thus, we estimate that the internal pressure is $\sim 50\text{ GPa}$.

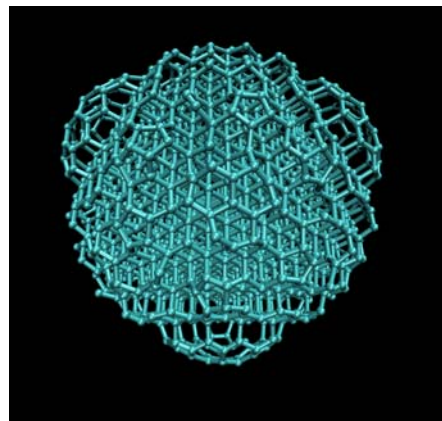


Figure 4. Equilibrated ND particle used in the collision studies

Quantum molecular dynamics (QMD) simulations were then performed on such two bare, reconstructed ND subjected to hypervelocity non-central collisions in order to explore conditions in which the outer shells could be disrupted and its subsequent effect.

The simulation involved an off-center high velocity collision of two NDs moving relative to one another at 20 km/sec . Figure 5 shows a series of sequential snapshots of colliding NDs during this trajectory from two perspectives: The left-most frames shows the NDs moving into or out of the plane of visualization. The right-most frame shows the NDs moving along the horizontal axis of the visualization.

Upon collision, shock waves propagate through the bodies of the NDs, and amorphization of the material at the contact region occurs as seen in Fig. 5 ($t=0.076\text{ ps}$). As is apparent in the right-most frame of the snapshot at 0.15 ps , (second frame), each ND shears and compresses material from the other in the region of direct collision of the two particles, leading a configuration of the two conjoined particles that resembles an “S”. At $t=0.20\text{ ps}$ (third frame), the two fragments separate, and we see the initial relaxation (expansion) of the region of the material that has been sheared and the ejection of small fragments (ranging from atoms to small carbon clusters) into the vacuum. The fourth frame, depicting the system at 0.359

ps, shows a continuing separation of the particles, with the various polyatomic moieties departing from the sheared region of the NDs into the vacuum.

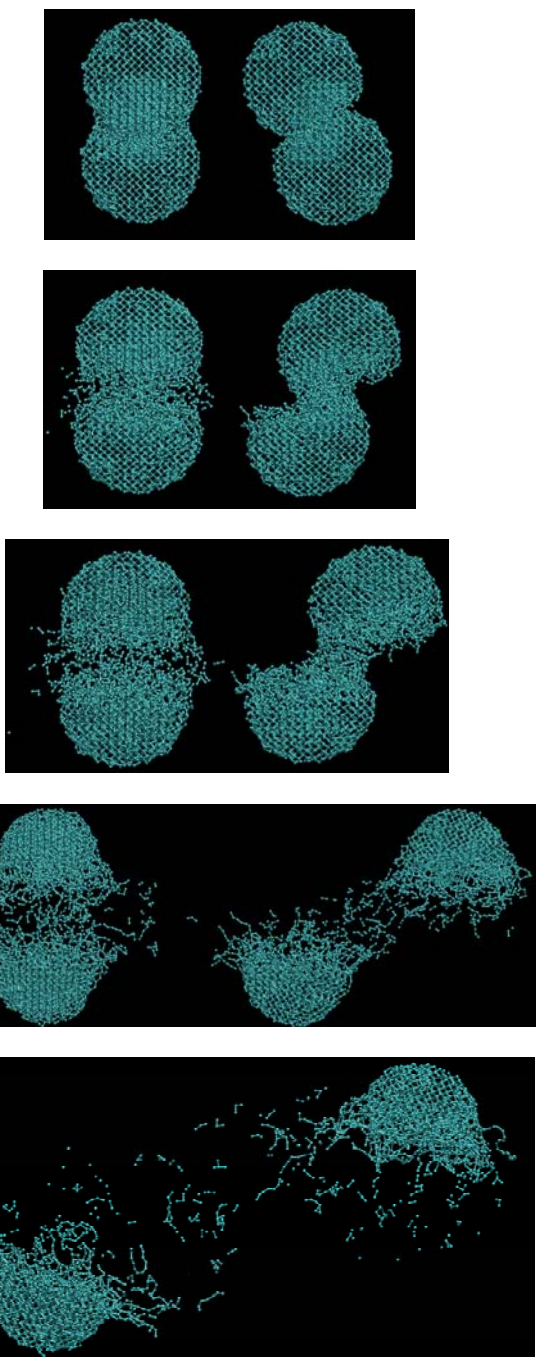


Figure 5. Snapshot of colliding NDs at 0.076 ps (top), 0.15 ps (second frame), 0.20 ps (third frame), 0.359 ps (fourth frame), 0.589 ps (bottom frame). All but the bottom frame show the collision from two perspectives; the snapshot at 0.589 ps only shows the collision moving along the horizontal axis of visualization. (see text).

The material at the sheared region of the fragments expands in all directions, leading to a deformation of the parent fragment in the region of the material. The bottom frame, corresponding to $t=0.589$ ps, shows that the fragments are continuing to expand and flatten relative to the original spherical shape. Additionally, the fragments are rotated relative to their initial arrangement about their inertial axes, indicating that during the collision, the fragments gain angular momentum. Animation of the snapshots for the duration of the trajectory show that the atoms on the entire surface of the retreating fragments are mobile and the surface material appears unstable. We are in the process of further exploring the behavior of these retreating fragments, as well as exploring these collisions at lower relative collision velocities (10 and 5 km/sec).

It is quite apparent from these simulations that high velocity collisions indeed disrupt the ND which subsequently comminutes into mono and multi-atomic fragments that are moving at high velocities and that are probably highly reactive. Such high-velocity reactive particles, when coming into contact with atmospheric gases would result in combustion, thus providing significant energy release. We intend to introduce molecular oxygen into a subsequent series of simulations in order to explore this possibility.

CONCLUSIONS

The above theoretical results indicate that ND could be potential sources of Structure Bond Energy for potential use as next generation energetic materials; however, the key to its use appears to be in the sudden rupture of the surface. Unlike the idealized ND explored in our theoretical study, nanodiamond particles produced by detonation synthesis have a composite structure comprised of a diamond core and an amorphous carbon outer shell. The outer shell thickness can be modified through various purification schemes and it is reasonable to expect variations in the SBER potential of nanodiamonds prepared under differing purification methods. Static high-pressure Raman spectroscopic measurements collected to 53 GPa showed a slight intensity increase in the OND feature near 1335 cm^{-1} which lies within the partial density of states of the diamond lattice. The intensification of this vibrational feature is consistent with a thinner amorphous carbon outer shell, which results in greater exposure to the diamond core under subsequent pressure increases. Exposure of the diamond core is thought to be an important precursor to SBER initiation. Additionally, a nearly two-fold increase in the vibrational intensity of the sp^2 graphite peak centered near 1630 cm^{-1} in the OND spectrum suggests the possibility of a sluggish partial phase transition from sp^3 -hybridized diamond to sp^2 -hybridized graphite. Future experiments will focus

on combining high-pressure with high-shear/strain conditions to judge whether the SBER phenomena can be triggered in nanodiamond materials. We expect that further theoretical and experimental investigations into the surface morphology and requirements to crack the shell will allow for a fundamental understanding of the conditions in which rapid release of this energy can be used.

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